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(54) Impregnated activated carbon

(57) An adsorbent material capable of chemisorbing hydrogen cyanide from a gaseous mixture which consists of a granular or fibrous activated carbon having impregnated thereon a transition metal salt of a non-chelating carboxylic acid. The transition metal salt preferably consists of cobalt, nickel or zinc acetate. The adsorbent material may be further impregnated with a silver salt and/or a cyclic amine (e.g. $AgNO_3$, pyridine, triethylenediamine). The adsorbent material may be used in respirators and like devices to remove HCN from the atmosphere.

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SPECIFICATION

Impregnated activated carbon

This invention relates to impregnated activated carbon and to methods for preparing impregnated activated carbon.

In the construction of gas masks (respirators), collective protectors and the like, a large variety of adsorbents have been suggested and used for removing the various types of harmful gases which may be encountered in chemical warfare. An adsorbent which has been used in the canisters of gas masks for the removal of poisonous gases such as hydrogen cyanide (HCN) has been activated charcoal (activated carbon) either containing or having impregnated thereon certain metals or metal compounds. The function of the metals or metal compounds is to break down the HCN by chemical reaction into harmless gaseous products and/or products which are readily physisorbed onto the activated carbon.

In the United Kingdom, the adsorbent which has been used for many years for the removal of HCN in particular is an activated charcoal which was formed by adding a copper containing compound to powdered coal whereafter the mixture was briquetted, carbonised, activated in high temperature steam, and graded to yield the final product. The charcoal could be and sometimes was subsequently treated with pyridine and silver (as $AgNO_3$) to provide protection against cyanogen chloride and certain arsenical agents. The charcoal thus prepared provided elimination of the poisonous gases by chemisorption. There are however several disadvantages in employing an adsorbent of this type. The chemisorption properties of the charcoal have been found to deteriorate over long periods of time. Since relatively large quantities of charcoal must be stored to be held in readiness for use in time of need, this problem has necessitated periodic regeneration of the charcoal, which is an expensive and time consuming process. A further serious disadvantage of this charcoal is that its production from a mixture of coal and copper-containing compound results in a great deal of wastage. Thus as much as 40% by weight of the starting material is lost as unusable fines which are essentially charcoal of carbon-containing copper. This loss is made all the more serious because the waste fines cannot be recycled and have no use. Their production therefore increases the cost of the useful charcoal product.

Many of the problems associated with briquetted carbons may be overcome by providing adsorbents prepared by impregnating activated charcoal with two or more metal salts (especially Cu^{2+} and Cr^{6+} salts) from solution, and subsequently drying the charcoal. An important group of adsorbents of this type, known as the whetlerite charcoals and described in, for example, US Patent Nos 1519470 (Wilson *et al*), 2920050 (Blacet *et al*), and and 2920051 (Wiig *et al*), are prepared by impregnating activated charcoal with ammoniacal solutions containing copper carbonate and other metal salts. Although whetlerite charcoals are claimed to remain effective against HCN after long periods of storage in conditions of high temperature and humidity, impregnated charcoals in general are susceptible to loss of effectiveness under these conditions and whetlerite charcoals themselves have the disadvantage that they can release a stong ammonia odour which is undesirable for use in respirators.

An additional disadvantage of known impregnated activated charcoals (including the whetlerite charcoals) is that normally they must be impregnated with more than one metal or metal salt in order to adsorb HCN effectively. For example, copper or copper salts are effective in oxidising HCN either to harmless gaseous products or to products which may be readily adsorbed by the charcoal. However, appreciable amounts of HCN are oxidised to cyanogen ($(CN)_2$), a toxic gas which (like HCN) is not readily adsorbed by activated charcoal. Chemisorption of $(CN)_2$ generated by the copper has to be effected by one or more further impregnants, such as chromate or a dichromate. This requirement for a plurality of metals or metal salts on the charcoal leads to the difficulty that the uptake of each metal salt from solution may vary considerably from one type of charcoal to another. Therefore it is difficult to prepare adsorbents by this technique which contain an optimum balance of metal to provide maximum protection against HCN. This has been found a particular problem when attenpting to impregnate fibrous activated carbons.

It is an object of the present invention to provide an impregnated activated carbon and a method for the preparation thereof in which the above disadvantages are overcome or at least mitigated in part.

According to a first aspect of the present invention there is provided an adsorbent material capable of removing HCN from a gaseous mixture, which comprises an activated carbon having impregnated thereon at least one transition metal salt of a non-chelating carboxylic acid.

The at least one metal salt is preferably a salt of a mono- or di-carboxylic acid, particularly a mono-carboxylic (for example an alkanoic) acid. The monocarboxylic acid is preferably a C_1-C_4 alkanoic acid, with acetic acid being most preferred. The cation of the at least one metal salt is preferably selected from ions of elements in the transition series of the first long period and from ions of transiti n metal elements in Group 2B and 8 of the Periodic Table, and is m st pr ferably selected from C $^{2+}$, Ni^{2+}, and Zn^{2+}. Th at least one metal salt is most preferably cobalt acetate or nickel acetate, which are found to give the best protection against HCN when impregnated onto activated carb n.

While the metal carboxylate can be supp rt d n th activated carb n in an am unt up to about 50% by weight, based on the total weight of the final product, when the final product is used as an agent for removing the above described gases, it is pref rably supported in an am unt of from about 0.1% by w ight to 30% by weight, and preferably from about 1% by weight to 20% by weight. When it is supported in amounts less than

0.1% by weight, the effect as a removal agent is insufficient whereas in amounts greater than 30% by weight, a decrease in the absorptive capacity f th carbon is bserv d, probably due to clogging f the por s within th carbon by solid metal carboxylat . The apparent specific surface area f the impr gnated activated carbon is preferably $500m^2/g$ or more, more preferably $800m^2/g$ or more. Preferably, the activated carbon has only one metal carboxylate impregnated thereon.

The activated carbon may be in any suitable form prepared by any number of known processes. It may be a granular activated carbon derived from, for example, a suitable coal or nut shell, or it may be fibrous activated carbon derived from, for example, fibres of acrylonitrile-based polymers, natural cellulose (such as cotton), regenerated cellulose (such as viscose rayon), phenolaldehyde resins, or pitch. A fibrous activated carbon is preferably in the form of a tow, felt, fabric (eg cloth) yarn, weave, web etc, because this type of carbon is becoming increasingly important for many commercial and military applications in view of its strength and high adsorptive capacity.

The fibrous activated carbon on which the metal carboxylate is to be supported desirably has a specific surface area, as measured by the BET method, of from about $600m^2/g$ to $2,000\ m^2/g$, and preferably from about $700m^2/g$ to $1,500m^2/g$. On fibrous activated carbons having specific surface areas of less than about $600m^2/g$, the fibrous activated carbon with the metal carboxylate supported thereon is of insufficient capacity to remove toxic substances effectively. On the other hand, those fibrous activated carbons having specific surface areas of more than about $2,000m^2/g$ are low in strength and are subject to limitations of usefulness.

Further, it is preferred from the standpoint of handling that the fibre diameter be from 3 to 25 microns. When the fibre diameter is less than 3 microns the fibre is easily cut during the production of activated carbon, and in molding in a felt form, it is difficult to obtain a web with ease. On the other hand, when the fibre diameter is more than 25 microns the activation thereof can be attained only with difficulty, and even if it is possible to obtain activated carbon having a predetermined specific surface area, it is difficult to obtain those activated carbons having high strengths because the activation yield is reduced.

The activated carbon may additionally be impregnated with other metallic and/or inorganic impregnants which provide for elimination of a wider range of toxic gases. One example of an additional impregnant is silver or a salt thereof (eg silver nitrate), preferably present on the activated carbon in the % weight range of 0.1 to 15%, most preferably 1 to 10%, which has been found to assist in the elimination of certain gaseous arsenical agents. A further example of an additional impregnant is an organic compound selected from the organic amines, especially the cyclic amines, preferred examples of which are pyridine and (most preferably) triethylenediamine (TEDA). These amines are found to assist in the elimination of toxic gases such as cyanogen chloride, and are preferably present on the activated carbon in the % weight range of 0.1% to 20%, most preferably 0.5% to 10%.

According to a second aspect of the present invention there is provided a method of preparing an adsorbent material which comprises providing an activated carbon, wetting the activated carbon with a solution of at least one transition metal salt of a non-chelating carboxylic acid, and drying the wetted activated carbon to provide an activated carbon impregnated with the at least one salt.

In order to wet the activated carbon with the dispersion or solution, the at least one transition metal carboxylate is preferably dissolved in water. Organic solvents which are liquid at ordinary temperature, have boiling points of not more than 100°C, and are easily driable may be used in place of water though these are less preferred. Such solvents include, for example, ketones such as acetone, and alcohols such as methanol and ethanol. The activated carbon may be wetted by soaking it in the solution by immersion or by spraying the solution onto the carbon, and is then dried. The concentration of the solution is generally from about 0.1wt% to about 30wt%, preferably 1 to 20wt%. The soaking time is preferably from about 10 minutes to about 1 hour. The drying is carried out at a temperature below the decomposition temperature of the metal carboxylate and generally at about 200°C or less.

The activated carbon may additionally be impregnated with one or both of a silver salt (preferably silver nitrate) and an organic amine, preferably a cyclic amine such as pyridine, most preferably TEDA. For either impregnant, impregnation is effected by wetting the activated carbon with a solution of the impregnant, and subsequently drying the carbon. It is essential that impregnation with one or both of these impregnants is carried out prior to wetting with the solution of the at least one transition metal carboxylate so that these impregnants do not upset the performance of the carboxylate. Where both impregnants are used, then the activated carbon is preferably impregnated with the organic amine followed by the silver salt followed by the at least one transition metal carboxylate. The concentration of the organic amine or silver salt in their respective solutions will generally be from 0.01 to 10 weight %, preferably from 0.1 to 5 weight %.

Activated carbons usually contain traces of inorganic compounds, especially chlorides, left over from their manufacture and the presence of these compounds can have a detrimental effect on the successful impregnation of th carbon with silver salts. Wh re pre-impr gnati n with a silver salts is mployed, in order to remove th se inorganic c mpounds the carbon is pref rably first treated with an aqueous solution of a str ng acid before any impregnation step. The pH of the solution is preferably less than one, and is most preferably less than z ro. A pref rred acid is nitric acid. H wever treatment with strong acid solutions is found to result in some oxidation and hydroxylation of the surface of the carbon, which has been found to result in increased cyanogen formation on the surface of the carbon when challenged with HCN. On the other hand, tr atment of th carbon prior to impregnant with an aqueous solution of a strong base is also preferred becaus it is found to enhance the subsequent uptake by the carbon of impr gnants from solution, although

it has little effect on the presence of inorganic impurities in the carbon. The pH of the base solution is preferably more than 13, most preferably mor than 14, and th base is preferably an alkali metal hydroxide, especially NaOH. Most preferably, however, the carbon is pre-treated first with the aque us solution of the strong base and then with the aqueous solution of the strong acid. Treatment with the strong base prior to the strong acid is found to improve impregnant uptake and to reduce the undesirable effects on the carbon of the strong acid. The carbon is preferably washed with water to remove residual acid or base thereon before impregnation commences.

The main advantage of the present adsorbent is that by employing only single salt impregnation it can provide an effective HCN chemisorbent without the associated generation of substantial quantities of cyanogen. Since little or no cyanogen is generated, the use of possibly carcinogenic chromium salt impregnants can be avoided if desired. The present impregnated products appear to retain their capacity to remove HCN even after prolonged storage under conditions of relatively high temperature and humidity, and since ammoniacal solutions are not necessarily used during their preparation, the unpleasant release of ammonia vapour from their surfaces can be avoided. Furthermore, the subsequent use of transition metal carboxylate impregnants over other impregnants such as silver salts and amines does not appear to interfere unduly with the ability of these other impregnants to assist in the remove of toxic gases other than HCN.

Although the invention is not in any way limited by this explanation, it is believed that HCN removal is particularly effective using the impregnated adsorbent of the invention because the bond between transition metal cations and non-chelating carboxylic acid anions are easily ruptured (and so are susceptible to chemical attack) to form very much more stable transition metal - cyano complexes. This effect appears to be most marked with cobalt acetate and nickel acetate.

Examples of impregnated activated carbons and of methods for their preparation in accordance with the present invention will now be described. In each Example, the carbon used was an activated carbon cloth prepared from woven viscose rayon cloth in accordance with the example given in UK Patent No 1310011. The carbon cloth had a BET surface area in excess of $600 m^2 g^{-1}$.

Impregnation - general procedure

Strips of dry activated carbon cloth were weighed and were then dipped for 30 to 40 minutes in an aqueous impregnating solution at 15 - 25°C containing a known concentration of metal carboxylate impregnant. The strips were then removed from the solution, lightly pressed between two sheets of clean blottong paper, and dried in air at a particular temperature for at least 12 hours. The drying temperature generally established whether the impregnant was present on the cloth in its hydrated form (eg $Co(OOCCH_3)_2.4H_2O$), which was generally the case when drying was performed at less than 40°C, or in its anhydrous form when drying was performed at higher temperatures. The impregnated cloth was then weighed again to establish the loading of the impregnant on the cloth.

Examples 1 to 25

25 examples of activated carbon cloth were impregnated with various impregnants in accordance with the General Procedure outlined above. The actual conditions of impregnation, and the amount of impregnant loaded onto the cloth after impregnation, are given in Table 1 below.

Of the carboxylates used, the acetates and nickel formate were taken as general purpose reagents, and the other salts prepared by reaction of metal carbonates with the appropriate acid in aqueous solution, with crystallization of the product. All of the samples for which results are quoted were prepared by dipping in aqueous solutions of the salts.

Example 25 is included for the purpose of comparison as an activated carbon impregnated with a carboxylate of a non-complexing metal.

Table 1

Example	Carboxylate Impregnant	Solution Concentration % w/v	Drying Temp. °C	Impregnant Loading on charcoal cloth (% weight)	
				%Total	%Metal
1	Cobalt Acetate	5	100	7.6	2.5
2	Cobalt Acetate	10	100	10.1	3.4
3	Cobalt Acetate	10	100	19.2	6.1
4	Cobalt Acetate	10	35	21.3	5.0
5	Cobalt Acetate	15	100	13.4	4.5
6	Cobalt Acetate	20	100	17.3	5.8
7	Cobalt Acetate	20	35	23.8	5.6
8	Cobalt Acetate	25	100	20.0	6.7
9	C balt Acetate	30	100	27.3	9.1
10	Nickel Acetate	5	100	7.2	2.4

11	Nickel Acetate	10	100	12.1	4.0
12	Nickel Acetate	10	35	18.9	4.5
13	Nickel Acetate	15	100	15.5	5.1
14	Nickel Acetate	20	100	17.2	5.7
15	Cobalt Formate	5	35	3.2	1.0
16	Nickel Formate	3	100	0.1	1.0
17	Nickel Formate	3 (sprayed)	35	16.7	5.3
18	Cobalt Propanoate	5	35	14.1	
19	Cobalt Propanoate	10	100	17.5	
20	Nickel Propanoate	5	35	13.3	
21	Nickel Propanoate	10	100	20.9	
22	Zinc Formate	5	35	8.0	2.7
23	Zinc Acetate	5	35	13.4	4.0
24	Zinc Acetate	10	35	18.8	5.6
25	Sodium Acetate	10	35	15.4	2.6

Example 26 (comparative)

Strips of unimpregnated activated carbon cloth were water-washed and dried.

Example 27

Strips of activated carbon cloth were dipped in a 0.4% (w/v) aqueous solution of triethylenediamine (TEDA) for 10 minutes, lightly pressed between two sheets of blotting paper, and dried at 100°C in air for at least 12 hours. TEDA loading on the cloth was measured at 2.5% by weight. The cloth was then impregnated with cobalt acetate in accordance with the General Procedure given above. The acetate solution concentration was 20%, and the air drying temperature 100°C. Cobalt acetate loading on the cloth was measured at 16% by weight, equivalent to 5.3% by weight cobalt.

Example 28

The procedure of Example 8 was repeated, after which the impregnated cloth was urged in air for 14 days under the artificially severe conditions of 80% relative humidity (80%R.H.) at 60°C.

Example 29

Strips of activated carbon cloth were dipped for 2 hours at 15°C in a 2M aqueous solution of sodium hydroxide. The strips were then thoroughly washed in distilled water and then impregnated with cobalt acetate in accordance with the procedure of Example 5. The loading of cobalt on the cloth was calculated asd 7.9% by weight.

Example 30

The procedure of Example 29 was repeated, after which the impregnated cloth was aged in air for 14 days at 60°C, 80% relative humidity (80%R.H.)

Example 31

Strips of activated carbon cloth were dipped in a 10% (w/v) methanolic solution of cobalt acetate tetrahydrate. Impregnant loading resulting after drying at 100° was 9.3% total (3.1% Co).

Example 32

Strips of activated carbon cloth were dipped in a 0.5% (w/v) aqueous solution of silver nitrate for 10 minutes, partially dried on blotting paper, and then dried in the air at 35°C for more than 12 hours. The loading of the silver nitrate on the cloth was measured at 6.9% by weight. The cloth was then impregnated with cobalt acetate in accordance with the General Procedure given above, employing a 15% (w/v) impregnating solution concentration and a drying temperature of 100°C. Cobalt acetate loading on the cloth was measured at 11.9% by weight, equivalent to 4.0% by weight cobalt.

Example 33

The procedure of example 32 was followed, except that prior to the silver nitrate dipping, the following additional steps were taken. The cloth was first dipped in a 5M solution of nitric acid and agitated frequently over a period of 30 minutes. The cloth was then removed and then thor ughly washed to remove all trace of acid. The cloth was then dipped in a 0.4%(w/v) aqueous solution of TEDA for 20 minutes, partially dried on blotting paper, and then air dried at 100°C. TEDA uptake n the cloth r sulted in a l ading f 4.3% by weight. Silver nitrate and cobalt acetate loadings wer measur d later in the proce dings at 5.1% and 10.7% by weight respectively.

Example 34 (comparative)

An activated carbon cloth impregnated with the conventional impregnants copper and chromium were prepared by the foll wing procedure. Strips of activated carbon cloth were dipped in a 5% (w/v) aqueous

solution of copper nitrate for 20 minutes, partially dried on blotting paper, and heated in a vertical furnace under reducing conditions to reduce the impregnant to copper metal. The strips were then dipped in a 7.5% (w/v) solution of sodium dichromat , partially dried on blotting paper, and then dried in air at 35°C f r at l ast 12 hours.

Example 35 (comparative)

The procedure of example 34 was repeated, after which the impregnated cloth was aged for 35 days in air at 60°, 20 - 30% relative humidity.

Samples of impregnated activated carbon cloth prepared in accordance with the Examples quoted above were tested for their ability to withstand a standard challenge of gaseous hydrogen cyanide in humid air. Prior to the test, cloth samples were equilibrated in an atmosphere maintained at 80% R.H. by a saturated salt solution. In each test, 20 layers of 2cm diameter of the humidified impregnated cloth were placed within a brass tube with mesh ends, and challenged with 1 $l.min^{-1}$ (1 = litre) of air at ambient temperature and pressure and 80-85% R.H., containing 2 $mg.l^{-1}$ hydrogen cyanide. The testing stream was passed through the bed perpendicular to the plane of the cloth layers, the effluent stream sampled every 2 minutes by an automatic valve, and passed to a gas chromatograph fitted with a flame ionization detector to detect the presence of HCN and $(CN)_2$. For each impregnated carbon, the time taken before at least $2 \times 10^{-6} g.l^{-1}$ of these gases appeared in the effluent gas was measured and recorded as the breakthrough or retention time of the bed tested.

For metal acetate impregnated samples, it was found that the HCN concentration rose steadily towards the applied $2mg.l^{-1}$ level once breakthrough had occurred. $(CN)_2$ production was infrequently observed with these samples, and in such cases levels were generally below 15 ppm, compared with 400-500 ppm for conventional copper-dichromate impregnated cloths. The generation of $(CN)_2$ levels often up to 30 ppm by unimpregnated cloth suggests that the carboxylates have no part in its generation, the cause of which is probably reaction of HCN with charcoal surface oxygen species and/or impurities present.

The results of the tests described above for the sample preparations are given in Table 2.

Table 2

Example (*comparative examples)	Breakthrough (retention) Times on HCN Gas Challenge (minutes) HCN	$(CN)_2$
1	17	
2	20	
3	29	
4	25	
5	28	
6	32	
7	20	
8	31	
9	11	
10	12	2
11	23	
12	29	20
13	23	
14	20	4
15	11	44
16	7	2
17	20	
18	23	
19	27	
20	20	
21	23	16
22	9	
23	8	
24	11	
*25	9	
*26	6	2
27	27	
28	24	
29	33	
30	13	
31	18	16
32	28	
33	23	

*34	18	12
*35	<2	<2

The results of Table 2 show:

(a) the advantages of Examples 1 - 24 over comparative Examples 25, 26, 34 and 35,
(b) the effects of increasing dip solution concentration on cloth loading and performance on testing,
(c) the advantage of pre-washing the charcoal in sodium hydroxide solution (see Examples 5,29),
(d) the effects of incorporating other desirable impregnants on to the charcoal along with the carboxylates, and
(e) the advantages of the present invention over other methods of charcoal impregnation (see Examples 34,35).

In addition to the test described above, the product of Example 27 was tested for its ability to withstand a standard challenge of cyanogen chloride. The test procedure was identical to that adopted for the HCN test, except that a 1 $l.min^{-1}$ stream of room temperature air at 70-75% relative humidity containing 2 $mg.l^{-1}$ cyanogen chloride was used instead. Effluent air, sampled for 5 seconds every 3 minutes, was analysed with a halogen detector to detect the presence of cyanogen chloride. Cyanogen chloride breakthrough was defined as the timed interval after which a level of more than $2 \times 10^{-6} g.l^{-1}$ cyanogen chloride was detected in the effluent gas. For the product of Example 27, this was found to be 23 minutes.

CLAIMS

1. An adsorbent material capable of removing HCN from a gaseous mixture, comprising an activated carbon having impregnated thereon at least one transition metal salt of a non-chelating carboxylic acid.
2. An adsorbent material according to claim 1, wherein the transition metal cation of the at least one salt is selected from ions of elements in the transition series of the first long period.
3. An adsorbent material according to claim 1 wherein the transition metal cation of the at least one salt is selected from ions of elements in Groups 2B and 8 of the Periodic Table.
4. An adsorbent material according to either claim 2 or claim 3 wherein the transition metal cation of the at least one salt is selected from the group consisting of Co^{2+}, Ni^{2+} and Zn^{2+}.
5. An adsorbent material according to any one of the preceding claims wherein the at least one salt is a salt of a mono- or di- carboxylic acid.
6. An adsorbent material according to claim 5 wherein the monocarboxylic acid is an alkanoic acid.
7. An adsorbent material according to claim 6 wherein the alkanoic acid is a C_1-C_4 alkanoic acid.
8. An adsorbent material according to claim 7 wherein the C_1 - C_4 alkanoic acid is acetic acid.
9. An adsorbent material according to claim 8 wherein the at least one salt is selected from the acetates of nickel, cobalt and zinc.
10. An adsorbent material according to any one of the preceding claims wherein the at least one transition metal salt is supported on the activated carbon in an amount of from 0.1% to 30% by weight of said carbon.
11. An adsorbent material according to any one of the preceding claims having an apparent specific surface area, as measured by the BET method, of at least $500 m^2 g^{-1}$.
12. An adsorbent material according to claim 11 having an apparent specific surface area, as measured by the BET method, of at least $800 m^2 g^{-1}$.
13. An adsorbent material according to any one of the preceding claims having one or more compounds, selected from a silver salt and an organic cyclic amine, additionally impregnated thereon.
14. An adsorbent material according to claim 13 wherein the silver salt is silver nitrate and the cyclic amine is pyridine or triethylenediamine.
15. An adsorbent material according to either claim 13 or claim 14 wherein the silver salt is supported on the activated carbon in an amount of from 0.1% to 15% by weight of the carbon.
16. An adsorbent material according to any one of claims 13 to 15 wherein the cyclic amine is supported on the activated carbon in an amount of from 0.1% to 20% by weight of the carbon.
17. An adsorbent material capable of removing HCN from a gaseous mixture substantially as hereinbefore described with reference to any one of Examples 1 to 24 and 27 to 33.
18. A method of preparing an adsorbent material capable of removing HCN from a gaseous mixture, which comprises the steps of

(a) providing an activated carbon;
(b) wetting th activated carbon with an impregnating solution of at least one transition metal salt of a non-chelating carboxylic acid; and
(c) drying the wetted activat d carbon to provide an activated carbon impr gnated with the at l ast one salt.

19. A method according to claim 18 wherein the transition metal cation f th at least ne salt is selected from ions f el ments in the transition series of the first l ng period.
20. A method according to claim 18 wherein the transition metal cation of the at least one salt is selected fr m ions of elements in Groups 2B and 8 of the Periodic Table.
21. A method according to claim 19 or 20 wherein the transition metal cation of the at l ast one salt is selected from the group consisting if Co^{+2}, Ni^{2+} and Zn^{2+}.

22. A method according to any one of the prec ding claims 18 to 21 wher in th at least one salt is a salt of a mono- or di-carboxylic acid.

23. A method according to claim 22 wherein the m nocarb xylic acid is an alkanoic acid.

24. A method according to claim 23 wherein the alkanoic acid is a C_1 - C_4 alkanoic acid.

25. A method according to claim 24 wherein the C_1 - C_4 alkanoic acid is acetic acid.

26. A method according to claim 25 wherein the at least one salt is selected from the acetates of nickel, cobalt and zinc.

27. A method according to any one of the preceding claims 18 to 26 wherein the concentration of the at least one salt in solution is from 0.1 weight % to 30 weight %.

28. A method according to any one of the preceding claims 18 to 27 wherein between step (a) and step (b) the activated carbon is wetted with one or more further impregnating solutions of impregnants selected from silver salts and cyclic amines, and is subsequently dried after wetting with each of the one or more further impregnating solutions.

29. A method according to claim 28 wherein the concentration of the impregnants in the one or more further impregnating solutions is from 0.01 to 10 weight %.

30. A method according to claim 28 or 29 wherein between step (a) and step (b) the activated carbon is wetted with a solution of a cyclic amine and is subsequently wetted with a solution of a silver salt.

31. A method according to any one of claims 18 to 30 wherein prior to wetting the activated carbon with any impregnating solution, the activated carbon is wetted with one or both of a basic solution having a pH greater than 13 and an acidic solution having a pH less than 1.

32. A method according to claim 31 wherein the activated carbon is wetted with the acidic solution followed by the basic solution.

33. A method of preparing an adsorbent material capable of removing HCN from a gaseous mixture, substantially as hereinbefore described with reference to any one of Examples 1 to 24 and 27 to 33.

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